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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08J 7/06, 7/12, D06M 10/04 // C08L 23:02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 96/30436</b> <b>(43) International Publication Date:</b> 3 October 1996 (03.10.96)
<b>(21) International Application Number:</b> PCT/NL95/00117 <b>(22) International Filing Date:</b> 27 March 1995 (27.03.95) <b>(71) Applicant (for all designated States except US):</b> DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ZAMOTAIEV, Pavel V. [UA/UA]; Kharkovskoe Shosse, 50, 559-7024, Kiev, 253160 (UA). CHODÁK, Ivan [SK/SK]; Zubekova 9, 941 01 Bratislava (SK). JACOBS, Martinus, Johannes, Nicolaas [NL/NL]; J. Van Maurikstraat 4, NL-6416 EH Heerlen (NL). <b>(74) Agent:</b> DERKS, Wilhelmus, Hubertus, Petrus; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		<b>(81) Designated States:</b> AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, US, UZ, VN, ARIPO patent (KE, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR THE MANUFACTURE OF A POLYOLEFIN SHAPED ARTICLE SHOWING IMPROVED CREEP PROPERTIES  <b>(57) Abstract</b> <p>The invention relates to a process for the manufacture of a creep resistant polyolefin shaped article wherein a highly oriented polyolefin shaped article is impregnated by vapor absorption with a volatile oxygen free halogenated derivative of carbon, sulphur, phosphor or silicon or combinations thereof as the UV-initiator and subsequently UV-irradiated to react the UV-initiator with the polyolefin.</p>		

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PROCESS FOR THE MANUFACTURE OF A POLYOLEFIN  
SHAPED ARTICLE SHOWING IMPROVED CREEP PROPERTIES

The invention relates to a process for the manufacture of a polyolefin shaped article wherein a highly oriented polyolefin shaped article is impregnated by vapor absorption with a UV-initiator and subsequently UV-irradiated to react the UV-initiator with the polyolefin. Further the invention relates to polyolefin shaped articles showing enhanced creep properties, fabricated articles comprising an assembled plurality of such polyolefin shaped articles and a process for the manufacture of said fabricated articles. With shaped articles in particular mono- or multifilament fibers or tapes are meant.

Highly oriented polyolefin shaped articles have the problem that they show a relatively high creep, where creep is meant to be a relative deformation (in particular elongation) under a force constant. This creep elongation presents the problem that the said articles are not suited for example for rope applications involving static loading. Part of the creep appears to be irreversible and the irreversible creep elongation, which accumulates with repeated loading during the service life of the article, presents the problem that the article has a lower than desired service life. Numerous different methods are described to improve the resistance to creep of highly oriented polyolefin shaped articles in order to overcome the abovementioned problems.

Chen and Ranby describe in Polymers for Advanced Technologies Vol. 1, p. 103-107 a process for the manufacture of a polyolefin shaped article possessing enhanced creep resistance wherein a highly oriented

polyolefin fiber is impregnated by vapor absorption with a UV-initiator and subsequently UV-irradiated to react the UV-initiator with the polyolefin. In this process benzophenone is used as the UV-initiator.

5           A disadvantage of this process is that it is required, in order to allow impregnation of the UV-initiator into the fiber, to impregnate at elevated temperatures (100°C). At this elevated temperature highly oriented polyolefin articles tend to shrink and to  
10       deteriorate in their mechanical properties. This can at least in part be prevented by keeping, in the known process, the fiber under constant strain to prevent shrinkage and loss of mechanical properties, which requires special equipment provisions.

15           The aim of the invention is to provide a process for the preparation of highly oriented polyolefin shaped articles possessing a better creep resistance than untreated articles that can be operated at a lower temperature than in the known process.

20           This aim is achieved by the invention in that the UV-initiator is a volatile oxygen free halogenated derivative of carbon, sulphur, phosphor or silicon or a combination of these compounds.

          It has been found that these UV-initiators  
25       according to the invention can be impregnated into the highly oriented polyolefin shaped article even at room temperature and that they, after UV-irradiation, significantly improve the creep resistance of the articles. Evidently the UV-initiator can also be  
30       impregnated into the article at higher temperatures with the advantage of a shorter impregnation time than in the known process.

          The term "UV-initiator" implies that the compound can be dissociated by UV radiation to form  
35       reactive parts which then react with the polyolefin. No further reactive substances are required to effect the creep resistance improvement. Preferably the halogen is

chlorine. It has been found that the halogenated compounds easily penetrate into a polyolefin shaped article if the halogenated compound is small. Preferably the largest cross-sectional dimension is below 200 nm, more preferably below 150 nm, even more preferably below 100 nm and most preferably below 80 nm.

In "Die Angewandte Makromolekulare Chemie 210", (1993) 119-128 (Nr. 3648) a process is disclosed in which a highly oriented polyolefin shaped article is impregnated by vapor absorption at a low temperature using  $\text{SO}_2\text{Cl}_2$  as the UV-initiator and is subsequently UV-irradiated. The document is however silent about the improvement of the creep resistance of the treated article. As described hereafter in Comparative experiment A it was found that a fiber treated with such an oxygen containing halogenated compound has a poor improvement of creep resistance and/or a poor retention of mechanical properties.

Very good results are obtained when the UV-initiator is an oxygen free halogenated hydrocarbon having 1-6 carbon atoms, sulphur halogenide, phosphorous halogenide or thiophosphoryl halogenide. Preferably the halogen is chlorine.

The most preferred UV-initiator is an oxygen free halogenated unsaturated hydrocarbon having 2 carbon atoms, for example  $\text{CHCl}=\text{CCl}_2$ . Polyolefin shaped articles that are treated with such a UV-initiator have a much lower creep rate and an almost complete suppression of the irreversible creep elongation. Further this UV-initiator is effective at a lower content.

Preferably the article comprises 0.1-10 w% (relative to the total weight of the article) of UV-initiator.

Highly oriented polyolefin shaped articles are for example described in GB-A-2,041,414, GB-A-2,051,667, US-A-4,413,110, US-A-4,551,296, EP-0,115,192 or WO-93/15118 and are characterised in that they have a high tenacity and a high modulus, typically a tenacity of at

least 1 GPa and a modulus of at least 35 GPa. In view of obtaining the highest possible creep resistance the polyolefin shaped article has preferably a tenacity of at least 2 GPa, more preferably at least 2.5 GPa and most preferably at least 3 GPa and a modulus of at least 50 GPa more preferably at least 80 GPa and most preferably at least 100 GPa.

The impregnation is preferably carried out by exposing the polyolefin shaped articles to the vapours of the volatile halogenated compound at a temperature below 30°C. The advantage of the low impregnation temperature is that the risk of shrinkage and the subsequent loss of mechanical properties is avoided and that the total amount of UV-initiator that is impregnated into the polyolefin shaped article can be higher. The impregnation time is 1-48 hours depending on the choice of the specific UV-initiator and the desired level of creep resistance. Very good improvement of creep resistance can be obtained by impregnation at room temperature for 15-30 hours. In particular, when using a halogenated hydrocarbon having 1 or 2 carbon atoms, a sulphur halogenide, a phosphorous halogenide or a thiophosphoryl halogenide the impregnation time is relatively short.

Evidently the UV-initiators may also be impregnated into the polyolefin shaped article at a higher temperatures with the advantage of a significantly shorter impregnation time than in case of the prior art UV-initiators. Preferably however the polyolefin shaped article is impregnated at a temperature below 80°C or preferably below 60°C to avoid shrinkage and loss of mechanical properties.

The process of impregnation and/or UV-irradiation may be repeated 1 to 3 times to obtain a further improvement of creep resistance. In a second treatment the temperature may be above 60°C or even above 80°C because due to the first treatment the temperature at which shrinkage occurs is raised.

Preferably the process is carried out in an inert or oxygenless atmosphere to avoid reaction of the UV-initiator or polyolefin in particular with oxygen.

The UV-irradiation is preferably carried out  
5 also below 30°C to avoid vaporisation of the UV-initiator out of the polyolefin shaped article. The irradiation time is preferably 1 to 10 minutes. The UV radiation preferably has a wavelength of 250-400 nm. It was found that with  
10 wavelengths below 250 nm in highly oriented polyolefin shaped articles chain scission occurs resulting in a decrease of mechanical properties. Above a wavelength of 400 nm the irradiation is less effective in dissociating the halogenated compounds.

The polyolefin shaped article may be subjected  
15 to a further stretching step between the impregnation with the UV-initiator and the UV-irradiation. Preferably however the article is UV-irradiated immediately after impregnation.

The invention further relates to a creep  
20 resistant polyolefin shaped article obtainable by a process according to the invention and to a creep resistant highly oriented polyolefin shaped article comprising a UV-initiator reacted with the polyolefin wherein the UV-initiator is a volatile oxygen free  
25 halogenated derivative of carbon, sulphur, phosphor or silicon or combinations thereof.

The creep resistance of the polyolefin shaped article of the invention is significantly improved. The creep resistance is quantified in the creep rate which is  
30 the relative elongation of the article per unit of time under a given load at a given temperature. Preferably, the creep rate is at most  $2 \cdot 10^{-8} \text{ s}^{-1}$  (as measured at 40°C under a 500 MPa load). Further it was found that the articles have an almost complete suppression of the irreversible  
35 creep elongation. Preferably the irreversible creep elongation at break (as measured at 40°C under a 500 MPa load) is at most 3%.

Preferably the creep rate is lower than  $1 \times 10^{-8}$   $s^{-1}$ , more preferably lower than  $6 \times 10^{-9}$   $s^{-1}$  and most preferably lower than  $3 \times 10^{-9}$   $s^{-1}$ . The irreversible creep elongation at break is preferably at most 2% and most  
5 preferably at most 1%. The total creep elongation at break is preferably less than 6%, more preferably less than 4% and most preferably at most 2%.

The polyolefin shaped articles of the invention have, in comparison with untreated polyolefin shaped  
10 articles, a number of further advantages like an improved heat resistance, an improved adhesion to polar substances, an improved abrasion resistance and a lower shrinkage on exposure to high temperature.

It was further found that, whereas the prior art  
15 methods rely with respect to improvement of creep resistance on a high gel content (typically above 80%), the creep resistant polyolefin articles of the invention can have a high creep resistance at a relatively low gel content. The gel content is a measure of the degree of  
20 crosslinking. In particular when sulphur halogenide a phosphorous halogenide or a thiophosphoryl halogenide is used as UV-initiator a significant improvement of creep resistance was obtained with a gel content of below 80% or even below 70%. From this it may be concluded that the  
25 improvement of creep resistance by the UV-initiators according to the invention is based on a different mechanism than the prior art methods. It is proposed that the improvement of the creep resistance is a combined effect of crosslinking (X-links) and grafting (Y-links) of  
30 the polyolefin chains. In the creep resistant polyolefin shaped article according to the invention the UV-initiator is reacted with the polyolefin to form X-links and Y-links preferably in a total amount between 0.1 and 10 per 1000 carbon atoms of the polyolefin. The amount of X-links and  
35 Y-links can be measured with  $C^{13}$  NMR as described by Fumitaka Horii e.a. in Macromolecules, 1990, 23, P.977-981.



The invention further relates to creep resistant fabricated articles comprising an assembled plurality of creep resistant polyolefin shaped articles according to the invention.

5           Fabricated articles are for example composite yarns, spun yarns, woven, knitted, plaited or braided textile fabrics, non-wovens, felts, ropes or fishing lines. The creep resistant fabricated articles according to the invention have a longer service life, have a lower  
10   creep elongation, a higher temperature resistance and further advantages as described above for the creep resistant polyolefin shaped article.

          A further aspect of the invention relates to a process for the manufacture of a creep resistant  
15   fabricated article as described above wherein a fabricated article comprising an assembled plurality of highly oriented polyolefin shaped articles is impregnated by vapor absorption with a volatile halogenated compound as the UV-initiator and is subsequently UV-irradiated to  
20   react the UV-initiator with the polyolefin. It was found that the highly oriented polyolefin shaped article has a very high transparency for UV-radiation, in particular in the wavelength range from 250 to 400 nm, and that hence also fabricated articles could be treated with the process  
25   of the invention. In this process the fabricated article preferably has a thickness of less than 5 mm, preferably less than 2 mm and more preferably less than 1 mm.

          The invention further relates to composite material comprising creep resistant polyolefin shaped  
30   articles or fabricated articles as described above. Such composites have an improved shear strength, delamination strength and temperature resistance.

          The invention is illustrated by the following examples.

Examples I-V

5 Ultrahigh molecular weight polyethylene fibers (Spectra 900<sup>R</sup> of Allied Signal Inc.) having a Young's modulus of 90 GPa and a tenacity of 2.8 GPa were wound on a quartz tube and placed in an exposure chamber. The chamber was connected to a closed flask containing the liquid UV-initiator. Both the chamber and the flask were at room temperature. The impregnation time was 24 hours. Subsequent to impregnation the samples were placed on a  
10 rotatable table that was placed in front of a DRT 1000 medium pressure Hg lamp. The samples rotated at 0.3 c/s. The radiation wavelength was between 243-363 nm. The distance from lamp to sample was 100-120 mm. The irradiation time was 3 minutes.

15 These preparations were repeated for several UV-initiators according to the invention as indicated in Table 1 (Examples 1 to 5). The creep rate was measured in a dead load creep rig at room temperature at loads of 0.5 GPa or 0.8 GPa during 100  
20 hours. The gel content was determined as the weight percent of undissolved polymer network after 48 hr extraction of the fiber in boiling xylene containing an antioxidant (0.5% Diaphen NN).

25

Table 1: Creep of fibers according to the invention  
(Examples I-V) creep rate ( $1/s \cdot 10^8$ )

Example	Initiator	Gel content (%)	0.5 GPa	0.8 GPa
I	$\text{CHCl}=\text{CCl}_2$	65.3	< 0.3	-
II	$\text{S}_2\text{Cl}_2$	5.3	< 0.3	1
III	$\text{PCl}_3$	42.5	-	0.6
IV	$\text{PSCl}_3$	17.6	-	< 1
V	$\text{CFCl}_3$ - $\text{CFCl}_3$	24.7	1.8	-

Comparative Experiment A-C

Examples I-V were repeated using oxygen containing halogenated compounds. The results of the fibers and of an unsaturated fiber are given in Table 2.

Table 2: Creep of fibers not according to the invention  
(Comparative Experiment A-C) creep rate  
( $1/s \cdot 10^8$ )

Comp. Exp.	UV-initiator	Gel content (%)	0.5 GPa	0.8 GPa
A	Untreated	0	6	10
B	$\text{SO}_2\text{Cl}_2$	48.9	6	6
C	$\text{CCl}_3$ - (C=O)- $\text{CCl}_3$	10.1	3	-

Examples VI-IX

The melting behaviour of the fibers under constraint was determined by fixing fibers of 0.2 m length on a metal frame. This frame was placed in an oven at 180°C for 1 min. All UV treated samples remained intact for at least 1 minute, while the untreated fibers (A) melted in seconds.

Ultra-high molecular weight polyethylene fibers of different draw ratio and hence different modulus were impregnated and UV treated using the procedure given above with a impregnation time of 48 hours and using  $\text{CHCl}=\text{CCl}_2$  as the UV-initiator. The creep properties were determined at a temperature of 40°C and a load of 0.6 GPa; the result was that for all fibers the irreversible creep was suppressed essentially completely. Table 3 gives the results.

Table 3: Creep properties fibers having different modulus treated with  $\text{CHCl}=\text{CCl}_2$

Example	VI	VII	VIII	IX
Modulus (GPa)	38	63	86	111
creep rate ( $1/\text{s} \cdot 10^8$ )				
$\text{CHCl}=\text{CCl}_2$	<50	<4	<0.2	~0.15
Untreated	300	30	10	6
Irreversible elongation at break (%)				
$\text{CHCl}=\text{CCl}_2$	<0.1	~0.2	<0.4	~0.4
Untreated	>11	>12	>13	>13

C L A I M S

1. Process for the manufacture of a polyolefin shaped article wherein a highly oriented polyolefin shaped article is impregnated by vapor absorption with a UV-initiator and subsequently UV-irradiated to react the UV-initiator with the polyolefin, characterised in that the UV-initiator is a volatile oxygen free halogenated derivative of carbon, sulphur, phosphor or silicon or combinations thereof.
2. Process according to claim 1, wherein the UV-initiator is an oxygen free halogenated hydrocarbon having 1-6 carbon atoms, a sulphur halogenide, a phosphorous halogenide or a thiophosphoryl halogenide.
3. Process according to claims 1 or 2, wherein the UV-initiator is a halogenated unsaturated hydrocarbon having 2 carbon atoms.
4. Process according to any one of claims 1 to 3, wherein the article comprises 0.1-10 w% (relative to the total weight) of UV-initiator.
5. Process according to any one of claims 1 to 4, wherein the article is impregnated at a temperature below 80°C.
6. Process according to any one of claims 1 to 4, wherein the article is impregnated at a temperature below 60°C.
7. Process according to any one of claims 1 to 6, wherein the article is impregnated and/or irradiated for 1 to 3 times.
8. Creep resistant polyolefin shaped article obtainable by a process according to any one of claims 1 to 7.
9. Creep resistant highly oriented polyolefin shaped article comprising a UV-initiator reacted with the polyolefin, characterised in that the UV-initiator is a volatile oxygen free halogenated derivative of carbon, sulphur, phosphor or silicon or combinations

thereof.

10. Creep resistant polyolefin shaped article according to claim 8 or 9 having a creep rate measured at 40°C under a 500 GPa load of at most  $2 \cdot 10^{-8} \text{ s}^{-1}$  and an irreversible creep elongation at break of at most 3%.  
5
11. Creep resistant polyolefin shaped article according to any one of claims 8 to 10 wherein the UV-initiator is reacted with the polyolefin to form X-links and Y-links in a total amount between 0.1 and 10 per 1000 carbon atoms of the polyolefin.  
10
12. Creep resistant fabricated article comprising an assembled plurality of creep resistant polyolefin shaped articles according to any one of claims 8 to 11.
- 15 13. Process for the manufacture of a creep resistant fabricated article in particular according to claim 12 wherein a fabricated article comprising an assembled plurality of highly oriented polyolefin shaped articles is impregnated by vapor absorption with a volatile oxygen free halogenated derivative of carbon, sulphur, phosphor or silicon or combinations thereof as the UV-initiator and subsequently UV-irradiated to react the UV-initiator with the polyolefin.  
20
- 25 14. Composite material comprising creep resistant polyolefin shaped articles according to any one of claims 8 to 11 or a fabricated article according to claim 12.
- 30 15. Polyolefin shaped articles, fabricated articles and composite materials as described in the description, examples and drawings.

# INTERNATIONAL SEARCH REPORT

Intern al Application No  
PCT/NL 95/00117

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08J7/06 C08J7/12 D06M10/04 //C08L23:02

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## B. FIELDS SEARCHED

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IPC 6 C08J D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 91-020697[03] & SU,A,1 565 857 (AS. UKR. PHYS. ORG. CHE.) 23 May 1990 see abstract ---	1,2,7-9
X	US,A,2 873 241 (STRZYZEWSKI 1.) 10 February 1959 see claims 1-3,5,6 see column 1, line 55 - line 65 ---	1-3
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 90-176463[23] & SE,A,8 802 943 (RANBY B. ET AL) 20 February 1990 see abstract --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

15 December 1995

Date of mailing of the international search report

29. 12. 95

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# INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/NL 95/00117

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 132 407 (MASSACHUSETTS INSTITUTE OF TECHNOLOGY) 30 January 1985 see claims 1,2,5,6 see page 4, line 10 - line 12 ---	1,2
A	CHEMICAL ABSTRACTS, vol. 80, no. 12, 25 March 1974, Columbus, Ohio, US; abstract no. 60590d, KATO,T. 'Surface modification of high molecular compound by UV irradiation in presence of fluorine-containing gas' page 29 ;column R ; see abstract & JP,A,47 047 854 (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.) 2 December 1972 -----	1,2



**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/NL 95/00117

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CA-A- 1248492	10-01-89
		DE-A- 3474677	24-11-88
		JP-A- 60076506	01-05-85
JP-A-47047854		NONE	

**PUB-NO:** WO009630436A1  
**DOCUMENT-IDENTIFIER:** WO 9630436 A1  
**TITLE:** PROCESS FOR THE MANUFACTURE  
OF A POLYOLEFIN SHAPED ARTICLE  
SHOWING IMPROVED CREEP  
PROPERTIES  
**PUBN-DATE:** October 3, 1996

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**APPL-NO:** NL09500117  
**APPL-DATE:** March 27, 1995

**PRIORITY-DATA:** NL09500117W (March 27, 1995)

**INT-CL (IPC):** C08J007/06 , C08J007/12 , D06M010/04

**EUR-CL (EPC):** C08J007/12 , D06M010/00 , D06M010/04 ,  
D06M010/06 , D06M010/08 , D06M014/28

**ABSTRACT:**

CHG DATE=19990617 STATUS=O>The invention relates to a process for the manufacture of a creep resistant polyolefin shaped article wherein a highly oriented polyolefin shaped article is impregnated by vapor absorption with a volatile oxygen free halogenated derivative of carbon, sulphur, phosphor or silicon or combinations thereof as the UV-initiator and subsequently UV-irradiated to react the UV-initiator with the polyolefin.